

The Conductivity, Temperature
Coefficients of Conductivity, and
Dissociation of Certain Electro-
lytes in Aqueous Solution
at 35°, 50°, and 65°.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CON-
FORMITY WITH THE REQUIREMENTS
FOR THE DEGREE OF DOC-
TOR OF PHILOSOPHY

BY
SAMUEL FRANCIS HOWARD

Baltimore, June, 1912

EASTON PA.:
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CONTENTS

	PAGE
Introduction.....	5
Historical.....	5
Experimental.....	8
Sodium Ferrocyanide.....	11
Potassium Carbonate.....	12
Potassium Permanganate.....	13
Di-potassium Phosphate.....	14
Potassium Sodium Sulphate.....	16
Potassium Chromium Sulphate (Violet).....	17
Potassium Chromium Sulphate (Green).....	16
Potassium Nickel Sulphate.....	19
Ammonium Chromium Sulphate (Violet).....	20
Ammonium Chromium Sulphate (Green).....	21
Calcium Bromide.....	22
Calcium Chromate.....	23
Zinc Nitrate.....	24
Zinc Acetate.....	25
Lead Chloride.....	26
Lead Acetate.....	27
Nickel Acetate.....	28
Uranyl Chloride.....	29
Uranyl Nitrate.....	30
Uranyl Sulphate.....	31
Uranyl Acetate.....	32
Hydrochloric Acid.....	33
Nitric Acid.....	34
Sulphuric Acid.....	35
Discussion.....	35
Summary.....	40
Biographical.....	42

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THE CONDUCTIVITY, TEMPERATURE COEFFICIENTS
OF CONDUCTIVITY AND DISSOCIATION OF
CERTAIN ELECTROLYTES IN AQUEOUS
SOLUTION AT 35°, 50° AND 65°

INTRODUCTION

Hosford and Jones,¹ and Miss Winston and Jones² have measured the conductivity, temperature coefficients of conductivity and dissociation of many electrolytes between 0° and 35°. To extend some of these measurements to higher temperatures, to ascertain whether certain observations made by them at lower temperatures obtain for higher temperatures, and to account, if possible, for certain discrepancies have been the aims of this investigation.

HISTORICAL

Conductivity measurements were made soon after Galvani's discovery of "animal electricity" (1789), and Volta's recognition (1793) of the two classes of conductors, one class conducting apparently without being changed chemically, while conductors of the second class were decomposed by the passage of the current.

Although the study of conductors of the second class did not, for many years, lead to a satisfactory explanation of the

¹ Am. Chem. J., **46**, 240 (1911).

² *Ibid.*, **46**, 368 (1911).

phenomena of conduction in solution, certain important relations were discovered.

Davy began investigations¹ in 1800 which led to the isolation of the alkali and alkaline earth metals and to the decomposition of water into hydrogen and oxygen. This work and that of others along the same lines led to the electrochemical theories of Davy² and Berzelius,³ and later to the announcement of Faraday's law.⁴

Faraday recognized that solutions of certain substances conducted the current, whereas those of others did not. The former he termed electrolytes and the latter nonelectrolytes. He saw, moreover, that the electrolytes decomposed into charged parts. Those parts which were charged negatively he termed anions, and those that were positively charged were called cations.

A large number of salts, acids and bases were studied by many workers, but the significance of conductivity was not understood until the theory of Arrhenius⁵ was proposed in 1887. This theory not only gave added interest and significance to the conductivity of solutions, but brought together under one generalization many of the abnormal measurements of osmotic pressure and of vapor tension and of freezing point lowering. The incentive to make conductivity measurements was greatly increased by the theory, especially as it was pointed out that dissociation could be measured when the conductivity was known at a given dilution and at infinite dilution.

That is, $\alpha = \mu_v / \mu_\infty$, where α is the dissociation, μ_v the conductivity at volume v , and μ_∞ the conductivity at complete dissociation or infinite dilution.

Since the measurements of conductivity can be interpreted in terms of the strengths of acids and bases, and since the reactions between various salts and acids, bases and other salts are conditioned by the amount of ionization, it is evident that a knowledge of these constants is desirable.

¹ Phil. Trans., 1807, 2.

² *Ibid.*, p. 39.

³ *Gilb. Ann.*, 27, 270 (1807).

⁴ *Exp. Researches in Elec.*, 1833-4.

⁵ *Z. physik. Chem.*, 1, 631 (1887).

The theory of solvation proposed by Jones¹ and confirmed by many lines of experiments conducted by him and his co-workers added further interest to conductivity measurements by explaining very satisfactorily, and for the first time, many apparent abnormalities.

Previous to the work of Kohlrausch,² conductivity measurements were made by means of direct currents, but because of polarization the results were not accurate. A considerable number of conductivity measurements have been made since the Kohlrausch method was proposed, but little systematic work was done until Jones and his coworkers took up the problem.

The work in this laboratory has been carried on systematically, measurements being made upon solutions of most of the more common electrolytes, at temperatures from 0° to 65°, and at convenient and uniform dilutions. When the work as a whole is completed there will be obtainable many data which have heretofore not been available.

¹ 1. Jones and Chambers: *Am. Chem. J.*, **23**, 89 (1900). 2. Chambers and Frazer: *Ibid.*, **23**, 512 (1900). 3. Jones and Getman: *Ibid.*, **27**, 433 (1902). 4. Jones and Getman: *Z. physik. Chem.*, **46**, 244 (1903); *Phys. Rev.*, **18**, 146 (1904). 5. Jones and Getman: *Am. Chem. J.*, **31**, 303 (1904). 6. Jones and Getman: *Z. physik. Chem.*, **49**, 385 (1904). 7. Jones and Getman: *Ber. d. chem. Ges.*, **37**, 1511 (1904). 8. Jones and Getman: *Am. Chem. J.*, **32**, 308 (1904). 9. Jones and Getman: *Ibid.*, **32**, 338 (1904). 10. Jones and Bassett: *Ibid.*, **33**, 534 (1905). 11. Jones: *J. chim. phys.*, **3**, 455 (1905). 12. Jones and Bassett: *Z. physik. Chem.*, **52**, 231 (1905). 13. Jones and Bassett: *Am. Chem. J.*, **34**, 291 (1905). 14. Jones: *Z. physik. Chem.*, **35**, 385 (1906). 15. Jones and McMaster: *Am. Chem. J.*, **35**, 136 (1906). 16. Jones: *Ibid.*, **35**, 445 (1906). 17. Jones and Uhler: *Ibid.*, **37**, 126 (1907). 18. Jones and Uhler: *Ibid.*, **37**, 244 (1907). 19. Jones and Pearce: *Ibid.*, **38**, 683 (1907). 20. Jones and Stine: *Ibid.*, **39**, 313 (1908). 21. Jones and Anderson: *P. Am. Phil. Soc.*, **47**, 276 (1908). 22. Jones and Jacobson: *Am. Chem. J.*, **40**, 355 (1908). 23. Jones: *Ibid.*, **41**, 19 (1909). 24. Jones and Anderson: *Ibid.*, **41**, 163 (1909). 25. Jones and Anderson: *P. Am. Phil. Soc.*, **48**, 194 (1909). 26. Jones and Strong: *Am. Chem. J.*, **43**, 37 (1910). 27. Jones and Strong: *Physik. Z.*, **10**, 499 (1909). 28. Jones and Strong: *Am. Chem. J.*, **43**, 224 (1910). 29. Jones and Strong: *Phil. Mag.*, **1910**, 566. 30. Jones: *Z. physik. Chem.*, **74**, 325 (1911). 31. Jones and Schmidt: *Am. Chem. J.*, **42**, 37 (1909). 32. White and Jones: *Ibid.*, **42**, 520 (1909). 33. Clover and Jones: *Ibid.*, **43**, 187 (1910). 34. White and Jones: *Ibid.*, **44**, 159 (1910). 35. West and Jones: *Ibid.*, **44**, 508 (1910). 36. Jones: *J. chim. phys.*, **9**, 217 (1911). 37. Winston: *Am. Chem. J.*, **45**, 547 (1911). 38. Wightman and Jones: *Ibid.*, **46**, 56 (1911). 39. Hosford and Jones: *Ibid.*, **46**, 240 (1911). 40. Winston and Jones: *Ibid.*, **46**, 368 (1911). 41. Jones: *Carnegie Inst. of Wash., Pub. No. 60* (1907). 42. Jones: *Ibid.*, No. **80** (1907). 43. Jones and Anderson: *Ibid.*, No. **110** (1909). 44. Jones and Strong: *Ibid.*, No. **130** (1910). 45. Jones and Strong: *Ibid.*, No. **160** (1911).

² *Wied. Ann.*, **6**, 145 (1879).

EXPERIMENTAL

Preparation of Material.—Kahlbaum's purest salts were used in nearly all cases, and were recrystallized several times from "conductivity water" prepared according to the method of Jones and Mackay.¹

Apparatus and Method.—The method of Kohlrausch was used, and the apparatus in general has been described by other workers in this laboratory. The bridge was of the Kohlrausch slide wire type, made and standardized by Leeds and Northrup, and graduated in half-millimeters. The cells are described by Clover and Jones² and by Jones and West,³ and the constants were determined every two weeks by means of a 0.02 N solution of potassium chloride, whose conductivity was taken as 129.7. A 0.002 N solution of potassium chloride was used for the cells whose plates were close together, its conductivity having been determined in a cell whose constant had been found by using the 0.02 N solution. Similarly, a 0.0005 N solution of potassium chloride was used to determine the constant for the water cell.

Because of the small conductivity of the water, as compared with that of even the most dilute solutions, a special "water cell" was used which differed from the other cells in having much larger electrodes. These electrodes consisted of two concentric cylinders of platinum from 2.5 to 2.75 inches high, held in position by small pieces of fusible glass, in such a manner that the inner and outer cylinders were a sixteenth of an inch or less apart.

Conductivity measurements were made at 35°, 50° and 65°, at the same dilutions as were used by other workers at the lower temperatures.

Two baths were employed, a smaller one for 35° and 65°, and a larger which was kept at approximately 50° day and night, and carefully adjusted for 50° during the measurements. When the cells were not in use they were kept in the larger bath in order to eliminate such changes in cell constants as

¹ Am. Chem. J., **19**, 91 (1897).

² *Ibid.*, **43**, 192 (1910).

³ *Ibid.*, **44**, 510 (1910).

would be produced by different temperatures. Each bath was made of galvanized iron, and consisted of two cylindrical vessels which were concentric, with asbestos cement between the vertical walls, and which had a common bottom.

The inner vessel for the smaller bath was 10 inches deep and 12 inches in diameter, while the outer was 10.5 inches deep and 16 inches in diameter. For the larger bath the inner vessel was 14 inches deep and 14 inches in diameter, the outer 14.5 inches deep and 18 inches in diameter.

"Asbestos wood" covers, $\frac{1}{8}$ inch thick, treated with a small amount of paraffin, were used on the baths. They were octagonal in shape, just large enough to extend over the rims of the outer vessel of each bath. Two circular holes, 2.25 inches in diameter, were cut in each cover, one in the center for the stirrer and thermometer, the other nearer the edge and over the line of cells supported in the bath. Brass guides were fastened to the edges so that the covers could be rotated upon the rims of the outer vessels.

The covers were cut and hinged so that the larger part was about two-thirds, and the smaller one-third of the whole. In the smaller part was the hole referred to, through which the wires were passed from the coil, etc., to each cell. The hole in the center was covered with a circular piece of asbestos wood, cut in two and fastened together after making small holes in it for the thermometer and stirrer. This did not revolve with the large cover.

Obviously the cover should be so constructed and fitted that as much heat as possible is retained in the bath with minimum evaporation of the water. On the other hand, it was necessary to remove the cells from time to time to inspect them and to eliminate air bubbles. It was also necessary to insert the wires into the cells and to change them to other cells. Thus, the cover must prevent loss of heat, and at the same time the cells must be accessible, and it is believed that these results were satisfactorily attained.¹

The gutta percha supports used for lower temperatures were

¹ Mr. E. J. Shaeffer and the author have been carrying on similar work, using the same cells and apparatus. Jointly they devised and constructed the accessories to the bath here described.

found to soften and warp at higher temperatures, and, therefore, supports made entirely of brass were used. Each holder supports three cells and the changes from one bath to another were made three cells at a time. If a bath was to be left at a certain temperature for a considerable time, a mercury thermostat was used, but usually a constant temperature was satisfactorily maintained within $0^{\circ}.01$ to $0^{\circ}.02$ by means of two low-form burners, one very small which could be carefully regulated, and the other to bring the bath rapidly to the correct temperature.

The cells were connected with a switch by means of a pair of pliable copper wires (No. 14) two or three feet long, and the switch in turn was connected with the other apparatus by larger wires.

Except for the modifications noted, the work was carried on similarly to that described by earlier workers.

Preparation of Solutions.—A few solutions were made by weighing out the purified salt and adding the correct amount of solvent. In most cases, however, a solution stronger than the strongest to be measured was made up and analyzed, and dilutions prepared from this.

The measuring apparatus was calibrated at 20° . When the "mother solution" was prepared, sufficient salt or salt solution was taken and placed in a measuring flask, and this was kept in the 50° bath for an hour and then water at the same temperature added to the mark. On cooling to 20° this was measured into the different burettes and flasks, and the desired volumes made up. The readings at 35° were multiplied by the factor 0.994 and those at 65° by the factor 1.0076.

Every one of the following results is the average of at least three measurements. A general discussion follows the tables:

Table I.—Sodium Ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$

The original solution was made by direct weighing of the anhydrous salt.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	306.61	386.89	469.609
16	330.29	418.91	508.689
32	380.43	487.25	593.800
128	457.93	594.44	727.678
512	554.43	730.35	909.856
1024	591.86	781.99	979.348
2048	614.64	804.49	1000.842
4096	633.20	803.01	968.996

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	5.35	1.74	5.51	1.42
16	5.89	1.78	5.99	1.43
32	7.12	1.87	7.10	1.46
128	9.10	1.98	8.88	1.49
512	11.73	2.11	11.90	1.63
1024	12.68	2.14	13.16	1.68
2048	12.66	2.06	13.09	1.63
4096	11.33	1.78	11.06	1.38

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	48.42	48.09	46.92
16	52.16	52.07	50.83
32	60.08	60.57	59.33
128	72.32	73.89	72.71
512	87.56	90.78	90.91
1024	93.47	97.20	97.85
2048	97.07	100.00	100.00
4096	100.00	99.82	96.82

Table II.—Potassium Carbonate, K_2CO_3

The original solution was made by direct weighing of the salt after heating for several hours at 110° .

<i>Molecular Conductivity</i>			
V	35°	50°	65°
2	158.35	199.34	228.63
8	191.45	237.57	291.17
16	216.87	278.66	341.86
32	228.87	296.51	369.42
128	263.89	340.18	424.50
512	284.36	378.64	468.12
2048	279.17	349.12	423.18
4096	253.01	314.61	376.53

<i>Temperature Coefficients</i>				
V	$35^\circ-50^\circ$		$50^\circ-65^\circ$	
	Cond. units	Per cent.	Cond. units	Per cent.
2	2.73	1.73	1.95	0.98
8	3.07	1.60	2.57	1.08
16	4.12	1.90	4.21	1.51
32	4.51	1.97	4.86	1.64
128	5.09	1.93	5.62	1.32
512	6.29	2.21	5.89	1.26
2048	4.66	1.66	4.94	1.17
4096	4.11	1.62	4.13	1.10

<i>Percentage Dissociation</i>			
V	35°	50°	65°
2	55.69	52.65	48.84
8	67.33	62.74	62.20
16	76.26	73.59	73.03
32	80.48	78.31	78.92
128	92.80	89.84	90.68
512	100.00	100.00	100.00
2048	98.17	92.20	90.40
4096	88.97	83.09	80.43

Table III.—Potassium Permanganate, KMnO_4

The permanganate solution was standardized volumetrically against potassium tetroxalate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	126.75	159.16	193.58
32	136.68	171.71	208.58
128	144.75	181.98	222.22
512	146.39	185.19	226.46
1024	145.39	182.45	215.95
2048	147.12	183.16	215.22
4096	146.26	178.59	205.22

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	2.16	1.70	2.29	1.44
32	2.32	1.70	2.46	1.43
128	2.48	1.71	2.68	1.47
512	2.59	1.77	2.75	1.48
1024	2.47	1.70	2.23	1.22
2048	2.40	1.63	2.14	1.17
4096	2.16	1.48	1.78	0.997

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	86.15	85.94	85.48
32	92.90	92.72	92.10
128	98.39	98.27	98.13
512	99.50	100.00	100.00
1024	98.82	98.52	95.36
2048	100.00	98.90	95.04
4096	99.42	96.44	90.62

Table IV.—Dipotassium Phosphate, K_2HPO_4

The original solution was standardized by determining the phosphoric acid as magnesium pyrophosphate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
2	139.86	175.07	212.29
8	184.28	234.37	285.21
32	221.75	285.70	350.72
128	252.43	321.93	396.74
512	290.51	346.06	427.15
1024	275.92	347.79	434.00
2048	268.44	344.92	432.97
4096	265.74	340.29	426.20

V	<i>Temperature Coefficients</i>			
	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
2	2.35	1.68	2.48	1.42
8	3.34	1.81	3.39	1.44
32	4.26	1.92	4.33	1.52
128	4.63	1.83	4.32	1.34
512	3.70	1.27	5.41	1.56
1024	4.78	1.73	5.75	1.65
2048	5.09	1.90	5.87	1.70
4096	4.97	1.87	5.73	1.68

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
2	48.14	50.34	48.91
8	63.43	67.39	65.72
32	76.33	82.15	80.81
128	86.89	92.56	91.42
512	100.00	99.50	98.42
1024	94.98	100.00	100.00
2048	92.40	99.17	99.77
4096	91.48	97.84	98.20

Table V.—Dipotassium Phosphate, K_2HPO_4

These readings were made *one month later* from solutions made up from the same mother solution as those of Table IV.

V	Molecular Conductivity		
	35°	50°	65°
2	197.54	247.08	298.51
8	315.66	401.01	487.30
32	334.60	427.58	519.59
128	372.53	478.50	590.59
512	414.08	533.40	659.24
1024	426.42	545.14	676.53
2048	422.17	545.44	671.96
4096			

V	Temperature Coefficients			
	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
2	3.30	1.66	3.43	1.39
8	5.66	1.79	5.75	1.43
32	6.20	1.85	6.14	1.44
128	7.07	1.90	7.45	1.56
512	7.95	1.92	8.39	1.57
1024	7.91	1.85	8.76	1.61
2048	8.22	1.95	8.43	1.55

V	Percentage Dissociation		
	35°	50°	65°
2	46.33	45.30	44.12
8	74.02	73.52	72.03
32	78.47	78.39	76.80
128	87.36	87.73	87.30
512	97.11	97.79	97.44
1024	100.00	99.95	100.00
2048	99.00	100.00	99.32

Table VI.—Potassium Sodium Sulphate, KNaSO_4

The solution was made by weighing the dry salt.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
4	182.65	225.23	272.73
8	199.55	251.17	305.40
32	237.05	301.65	367.39
128	270.35	345.97	424.23
512	291.20	375.47	455.59
1024	297.42	382.60	469.31
2048	307.87	395.50	489.05
4096	330.07	427.44	521.52

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.84	1.55	3.17	1.41
8	3.44	1.72	3.61	1.44
32	4.31	1.82	4.38	1.45
128	5.04	1.86	5.22	1.51
512	5.62	1.93	5.34	1.42
1024	5.68	1.91	5.78	1.51
2048	5.84	1.90	6.24	1.58
4096	6.09	1.85	6.35	1.46

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
4	55.34	52.69	52.30
8	60.46	58.76	58.56
32	71.82	70.57	70.45
128	81.91	80.94	81.34
512	88.22	87.84	87.36
1024	90.11	89.51	89.99
2048	93.17	92.53	93.77
4096	100.00	100.00	100.00

Table VII.—Potassium Chromium Sulphate (Violet),
 $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The original solution was standardized by determining the sulphuric acid as barium sulphate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	166.97	201.86	242.04
16	183.28	219.21	276.73
32	225.77	271.70	339.90
128	288.11	363.28	467.30
512	404.13	499.67	658.91
1024	465.44	586.07	785.37
2048	546.86	701.81	928.44
4096	637.39	818.02	1082.97

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units.	Per cent.	Cond. units	Per cent.
8	2.33	1.39	2.68	1.33
16	2.39	1.30	3.83	1.28
32	3.06	1.36	4.55	1.67
128	4.34	1.46	6.93	1.91
512	6.37	1.57	10.62	2.15
1024	8.04	1.73	13.29	2.27
2048	10.33	1.89	15.11	2.15
4096	12.04	1.89	17.66	2.16

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	26.20	24.68	22.35
16	28.75	26.80	25.55
32	35.42	33.21	31.39
128	46.77	44.41	43.15
512	63.40	61.08	60.84
1024	73.02	71.65	72.52
2048	85.80	85.79	85.73
4096	100.00	100.00	100.00

Table VIII.—Potassium Chromium Sulphate (Green)

This solution was made by heating the original violet solution at 80° for at least eight hours.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	193.98	221.47	248.10
16	219.16	252.44	279.35
32	270.38	318.16	352.59
128	357.98	437.81	485.99
512	474.89	618.30	699.33
1024	487.61	658.54	771.94
2048	535.90	753.80	903.28
4096	584.29	848.62	1017.05

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	1.83	0.94	1.78	0.80
16	2.22	1.01	1.79	0.71
32	3.19	1.18	2.30	0.72
128	5.32	1.49	3.21	0.73
512	9.56	2.01	5.40	0.87
1024	11.39	2.34	7.56	1.15
2048	14.53	2.71	9.97	1.37
4096	17.62	3.02	11.23	1.32

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	33.20	26.10	24.39
16	37.51	29.75	27.47
32	46.27	37.49	34.67
128	61.27	51.59	47.78
512	81.28	72.86	68.76
1024	83.45	77.60	75.90
2048	91.72	88.83	88.81
4096	100.00	100.00	100.00

Table IX.—*Potassium Nickel Sulphate*, $K_2Ni(SO_4)_2 \cdot 6H_2O$
 The sulphuric acid was determined as barium sulphate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	273.53	343.45	407.67
32	349.04	438.23	527.29
128	432.10	547.33	659.73
512	513.77	655.16	798.45
1024	545.16	695.98	850.21
2048	587.40	752.22	927.00
4096	607.93	785.94	960.54

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	4.66	1.70	4.28	1.25
32	5.95	1.70	5.94	1.36
128	7.68	1.78	7.49	1.37
512	9.43	1.84	9.55	1.46
1024	10.05	1.84	10.28	1.48
2048	10.99	1.87	11.65	1.55
4096	11.87	1.95	11.64	1.48

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	44.99	43.70	42.44
32	57.42	55.76	54.90
128	71.08	68.64	68.68
512	84.51	83.36	83.13
1024	89.68	88.55	88.51
2048	96.62	95.71	96.51
4096	100.00	100.00	100.00

Table X.—Ammonium Chromium Sulphate (Violet),
 $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The sulphuric acid was determined as barium sulphate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	169.80	204.92	244.97
16	197.87	239.15	288.79
32	228.59	274.46	333.50
128	302.72	369.58	459.09
512	410.17	508.79	648.99
1024	483.10	604.32	754.79
2048	577.37	713.72	897.35
4096	671.17	853.42	1050.26

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	2.34	1.38	2.67	1.30
16	2.75	1.39	3.31	1.38
32	3.06	1.34	3.94	1.44
128	4.46	1.47	5.90	1.60
512	5.91	1.44	9.35	1.84
1024	8.08	1.67	10.03	1.66
2048	9.09	1.57	12.24	1.71
4096	12.15	1.81	13.12	1.54

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	25.30	24.01	23.32
16	29.48	28.02	27.50
32	34.06	32.16	31.75
128	45.10	43.31	43.71
512	61.11	59.63	61.79
1024	71.98	70.81	71.87
2048	86.02	83.63	85.44
4096	100.00	100.00	100.00

Table XI.—Ammonium Chromium Sulphate (Green)

This solution was made by heating the original violet solution at 80° for at least eight hours.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	193.98	223.33	250.70
16	229.79	268.08	299.59
32	268.04	316.57	352.20
128	355.62	436.52	489.76
512	446.13	585.31	673.80
1024	492.16	658.87	789.57
2048	537.15	757.75	924.29
4096	589.81	868.79	1061.73

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	1.96	1.01	1.82	0.81
16	2.55	1.11	2.10	0.78
32	3.24	1.21	2.38	0.75
128	5.39	1.52	3.55	0.81
512	9.28	2.08	5.90	1.01
1024	11.11	2.26	8.71	1.32
2048	14.71	2.74	11.10	1.46
4096	18.60	3.15	12.86	1.48

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	32.89	25.71	23.61
16	38.96	30.86	28.32
32	45.45	36.44	33.17
128	60.29	50.24	46.13
512	75.64	67.37	63.46
1024	83.44	75.84	74.37
2048	91.07	87.22	87.06
4096	100.00	100.00	100.00

Table XII.—Calcium Bromide, CaBr_2

The calcium was determined as the oxide by ignition of the oxalate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
2	176.49	219.99	262.05
8	220.47	278.91	339.40
16	233.42	296.41	362.30
32	250.41	318.70	391.68
128	273.47	350.57	431.83
512	288.84	375.49	458.67
1024	300.23	386.64	477.18
2048	303.99	390.98	487.30

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
2	2.90	1.64	2.84	1.30
8	3.90	1.77	4.03	1.44
16	4.20	1.80	4.39	1.48
32	4.55	1.82	4.86	1.52
128	5.14	1.88	5.42	1.55
512	5.77	1.99	5.54	1.48
1024	5.76	1.92	6.03	1.56
2048	5.80	1.91	6.42	1.64

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
2	58.06	56.27	53.78
8	72.53	71.34	69.65
16	76.79	75.81	74.35
32	82.37	81.51	80.38
128	89.96	89.66	88.62
512	95.02	96.04	94.12
1024	98.76	98.89	97.92
2048	100.00	100.00	100.00

Table XIII.—Calcium Chromate, CaCrO₄

The mother solution was standardized by determining the calcium oxide from ignition of the oxalate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	128.60	158.03	187.81
16	145.08	180.02	214.73
32	163.29	204.40	243.98
128	207.22	261.25	315.84
512	247.52	315.98	387.01
1024	261.40	332.29	401.22
2048	269.70	344.41	418.31
4096	266.11	340.24	419.18

V	<i>Temperature Coefficients</i>			
	35°-50°		50°-65°	
	Cond. units.	Per cent.	Cond. units.	Per cent.
8	1.96	1.52	1.99	1.26
16	2.37	1.63	2.27	1.26
32	2.74	1.68	2.64	1.29
128	3.60	1.74	3.64	1.39
512	4.56	1.84	4.74	1.50
1024	4.73	1.81	4.60	1.38
2048	4.98	1.85	4.93	1.43
4096	4.94	1.86	5.26	1.55

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	47.68	45.88	44.80
16	53.79	52.44	51.23
32	60.55	59.35	58.20
128	76.83	75.85	75.35
512	91.78	91.75	92.33
1024	96.92	96.48	95.72
2048	100.00	100.00	99.79
4096	98.67	98.79	100.00

Table XIV.—Zinc Nitrate, $\text{Zn}(\text{NO}_3)_2$

The zinc was determined as zinc oxide.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
4	168.65	211.18	258.65
8	188.01	238.25	289.67
32	218.36	280.00	343.09
128	243.53	312.91	384.97
512	260.98	336.48	415.20
1024	267.95	347.35	428.50
2048	276.37	352.62	434.82
4096	281.02	359.97	445.53

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.84	1.68	3.16	1.50
8	3.35	1.78	3.43	1.44
32	4.11	1.88	4.21	1.50
128	4.63	1.90	4.80	1.53
512	5.03	1.93	5.22	1.55
1024	5.29	1.97	5.41	1.56
2048	5.08	1.84	5.48	1.55
4096	5.26	1.87	5.70	1.58

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
4	60.01	58.67	58.05
8	66.90	66.19	65.02
32	77.70	77.78	77.01
128	86.66	86.93	86.41
512	92.87	93.47	93.19
1024	95.35	96.49	96.18
2048	98.35	97.96	97.60
4096	100.00	100.00	100.00

Table XV.—Zinc Acetate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$

The zinc was determined as zinc oxide.

<i>V</i>	<i>Molecular Conductivity</i>		
	35°	50°	65°
8	77.18	90.46	100.61
32	122.60	149.28	172.86
128	162.36	205.63	243.46
512	188.21	242.85	298.49
1024	190.99	246.67	298.74
2048	198.90	257.81	319.47
4096	198.27	259.11	320.44

<i>V</i>	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	0.89	1.15	0.68	0.75
32	1.78	1.45	1.57	1.05
128	2.88	1.77	2.52	1.23
512	3.64	1.93	3.71	1.53
1024	3.71	1.94	3.47	1.41
2048	3.93	1.98	4.11	1.59
4096	4.06	2.05	4.09	1.58

<i>V</i>	<i>Percentage Dissociation</i>		
	35°	50°	65°
8	38.80	34.91	31.40
32	61.63	57.61	53.94
128	81.63	79.36	75.98
512	94.63	93.72	93.15
1024	96.02	95.20	93.23
2048	100.00	99.50	99.70
4096	99.68	100.00	100.00

Table XVI.—Lead Chloride, PbCl₂

The salt was dried and weighed directly.

<i>V</i>	<i>Molecular Conductivity</i>		
	35°	50°	65°
64	223.16	277.13	331.22
128	251.27	314.89	379.39
512	290.75	370.26	452.75
1024	305.58	387.25	476.90
2048	316.59	412.06	502.84
4096	326.33	416.97	515.18

<i>V</i>	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
64	3.60	1.61	3.61	1.30
128	4.24	1.69	4.30	1.37
512	5.30	1.82	5.50	1.49
1024	5.44	1.78	5.98	1.54
2048	6.36	2.01	6.05	1.47
4096	6.04	1.85	6.57	1.58

<i>V</i>	<i>Percentage Dissociation</i>		
	35°	50°	65°
64	68.39	66.46	64.29
128	77.01	75.52	73.64
512	89.11	88.80	87.88
1024	93.65	92.87	92.57
2048	97.03	98.82	97.60
4096	100.00	100.00	100.00

Table XVII.—Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$

The lead was determined as lead sulphate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
4	27.00	34.57	41.42
8	37.98	48.18	58.12
32	66.83	84.36	102.61
128	105.95	132.56	158.54
512	152.89	191.61	228.18
1024	170.98	214.38	255.53
2048	191.50	242.06	289.42
4096	204.87	260.97	315.50

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	0.51	1.89	0.46	1.33
8	0.68	1.79	0.66	1.37
32	1.17	1.75	1.22	1.45
128	1.77	1.67	1.73	1.31
512	2.58	1.69	2.44	1.27
1024	2.89	1.69	2.74	1.28
2048	3.37	1.76	3.16	1.36
4096	3.41	1.66	3.64	1.39

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
4	13.18	13.25	13.13
8	18.54	18.46	18.42
32	32.62	32.33	32.52
128	51.72	50.80	50.25
512	74.63	73.42	72.32
1024	83.46	82.15	80.99
2048	93.47	92.75	91.73
4096	100.00	100.00	100.00

Table XVIII.—Nickel Acetate, $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$

The nickel was determined as nickel oxide.

<i>V</i>	<i>Molecular Conductivity</i>			
	35°	50°	65°	
2	47.95	60.45	72.22	Hydrolysis
8	91.99	115.65	138.32	
16	114.02	144.47	171.27	
32	134.85	171.78	206.39	
128	172.52	223.26	272.67	
512	196.30	256.95	316.98	
1024	206.88	270.18	336.46	
2048	212.66	276.44	247.66	

<i>V</i>	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
2	0.32	1.73	0.78	1.29
8	1.58	1.72	1.49	1.29
16	2.03	1.78	1.79	1.24
32	2.56	1.90	2.31	1.34
128	3.38	1.96	3.29	1.47
512	4.04	2.06	4.00	1.56
1024	4.22	2.04	4.42	1.64
2048	4.25	2.00	4.73	1.71

<i>V</i>	<i>Percentage Dissociation</i>		
	35°	50°	65°
2	22.55	21.87	20.77
8	43.26	41.84	39.79
16	53.62	52.26	49.26
32	63.41	62.14	59.37
128	81.12	80.76	78.43
512	92.31	92.95	91.18
1024	97.18	97.74	96.78
2048	100.00	100.00	100.00

Table XIX.—*Uranyl Chloride*, $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$

The uranium in the chloride, nitrate, sulphate and acetate was precipitated with ammonia and weighed as the oxide U_3O_8 .

<i>V</i>	<i>Molecular Conductivity</i>		
	35°	50°	65°
4	160.71	198.60	234.14
8	181.31	227.96	272.75
32	217.37	278.17	339.88
128	244.66	316.71	392.84
512	270.65	353.32	445.64
1024	280.77	366.62	470.77
2048	289.83	384.32	487.43
4096	312.88	414.00	527.23

<i>V</i>	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.53	1.57	2.37	1.19
8	3.11	1.72	2.65	1.16
32	4.05	1.86	4.11	1.48
128	4.80	1.96	5.07	1.60
512	5.51	2.04	6.15	1.74
1024	5.72	2.04	6.94	1.89
2048	6.30	2.17	6.87	1.79
4096	6.74	2.15	7.55	1.82

<i>V</i>	<i>Percentage Dissociation</i>		
	35°	50°	65°
4	51.36	47.97	44.41
8	57.95	55.06	51.73
32	69.47	67.19	64.47
128	78.20	76.50	74.51
512	86.50	85.34	84.52
1024	89.74	88.56	89.29
2048	92.63	92.83	92.45
4096	100.00	100.00	100.00

Table XX.—Uranyl Nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
4	157.89	199.01	245.03
8	177.97	226.59	277.69
32	216.65	279.42	345.77
128	249.88	327.08	406.32
512	285.11	376.95	476.52
1024	304.61	404.71	514.08
2048	318.91	422.85	538.35
4096	349.78	467.92	596.77

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.74	1.74	3.07	1.54
8	3.24	1.82	3.41	1.50
32	4.18	1.93	4.42	1.58
128	5.15	2.06	5.28	1.61
512	6.12	2.15	6.64	1.76
1024	6.67	2.19	7.29	1.80
2048	6.93	2.17	7.70	1.82
4096	7.88	2.25	8.59	1.84

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
4	45.14	42.53	41.06
8	50.88	48.42	46.53
32	61.94	59.72	57.94
128	71.44	69.90	68.09
512	81.51	80.56	79.85
1024	87.09	86.49	86.14
2048	91.17	90.37	90.21
4096	100.00	100.00	100.00

Table XXI.—Uranyl Sulphate, $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$

<i>Molecular Conductivity</i>			
V	35°	50°	65°
8	158.81	179.79	197.94
32	201.03	223.69	240.24
128	158.21	288.77	309.93
512	333.38	381.83	416.68
1024	377.29	436.95	488.19
2048	428.71	512.04	582.85
4096	484.32	597.28	694.01

<i>Temperature Coefficients</i>				
V	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	1.40	0.88	1.21	0.67
32	1.51	0.75	1.10	0.49
128	2.04	0.79	1.41	0.49
512	3.23	0.97	2.32	0.61
1024	3.97	1.05	3.42	0.78
2048	5.49	1.28	4.72	0.92
4096	7.53	1.55	6.45	1.08

<i>Percentage Dissociation</i>			
V	35°	50°	65°
8	32.79	30.10	28.52
32	41.51	37.45	34.62
128	53.31	48.35	44.66
512	68.83	63.93	60.04
1024	77.90	73.16	70.34
2048	88.52	85.73	83.98
4096	100.00	100.00	100.00

Table XXII.—*Uranyl Acetate*, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ *Molecular Conductivity*

V	35°	50°	65°
8	50.15	63.14	77.48
32	66.36	82.48	99.33
128	86.21	106.30	126.95
512	109.30	132.66	156.86
1024	119.64	144.10	170.74
2048	131.55	158.30	185.97
4096	151.69	183.60	216.99

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	0.87	1.73	0.97	1.54
32	1.07	1.61	1.12	1.36
128	1.34	1.55	1.38	1.30
512	1.56	1.42	1.61	1.21
1024	1.63	1.36	1.78	1.23
2048	1.78	1.35	1.84	1.16
4096	2.13	1.40	2.23	1.21

Percentage Dissociation

V	35°	50°	65°
8	33.1	34.4	35.7
32	43.8	44.9	45.8
128	56.8	58.9	58.5
512	72.1	72.3	72.3
1024	79.2	78.5	78.7
2048	86.7	86.2	85.7
4096	100.0	100.0	100.0

Table XXIII.—Hydrochloric Acid, HCl

The original solution, made by passing a calculated amount of hydrogen chloride gas into "conductivity" water, was standardized against a solution of alcoholic potash which had been standardized against potassium tetroxalate (kindly furnished me by Dr. H. O. Eysell). The results agreed almost exactly with a determination of the chlorine gravimetrically as silver chloride.

Molecular Conductivity

V	35°	50°	65°
8	409.41	479.21	545.15
16	419.19	493.70	562.18
32	430.36	511.38	579.44
128	440.73	522.12	596.58
512	444.27	525.32	598.69
1024	434.68	510.79	585.20

Temperature Coefficients

V	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	4.65	1.14	4.40	1.92
16	4.97	1.19	4.57	0.93
32	5.40	1.25	4.54	0.89
128	5.43	1.23	4.96	0.95
512	5.43	1.22	4.89	0.93
1024	5.07	1.17	4.96	0.97

Percentage Dissociation

V	35°	50°	65°
8	92.15	91.22	91.06
16	94.35	93.98	93.90
32	96.87	97.35	96.78
128	99.20	99.39	99.65
512	100.00	100.00	100.00
1024	97.84	97.23	97.75

Table XXIV.—Nitric Acid, HNO_3

Standardized against the alcoholic potash which was used for hydrochloric acid (*q. v.*).

V	35°	50°	65°
4	366.32	428.63	472.54
8	386.08	454.51	511.18
16	399.13	466.54	529.08
32	412.37	486.24	553.20
128	421.25	499.17	569.97
512	425.26	503.90	577.82
1024	416.39	493.80	609.91

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	4.15	1.13	2.93	0.68
8	4.56	1.18	3.78	0.83
16	4.49	1.13	4.16	0.89
32	4.92	1.19	4.46	0.92
128	5.19	1.23	4.72	0.95
512	5.24	1.23	4.93	0.98
1024	5.16	1.24	7.74	1.57

Percentage Dissociation

V	35°	50°	65°
4	86.14	85.06	77.48
8	90.79	90.20	83.81
16	93.86	92.59	86.75
32	96.97	96.50	90.70
128	99.06	99.06	93.45
512	100.00	100.00	94.74
1024	97.91	97.99	100.00

Table XXV.—Sulphuric Acid, H_2SO_4

The acid was determined as barium sulphate.

V	<i>Molecular Conductivity</i>		
	35°	50°	65°
4	377.48	412.68	443.74
8	477.22	527.78	564.55
16	504.21	554.34	597.19
32	551.37	600.95	641.99
128	657.91	718.48	757.05
512	797.94	893.04	953.00
2048	862.33	998.08	1111.85
8192	892.55	1077.34	1203.92

V	<i>Temperature Coefficients</i>			
	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.35	0.62	2.07	0.50
8	3.37	0.71	2.45	0.46
16	3.34	0.61	2.86	0.52
32	3.31	0.60	2.74	0.46
128	4.04	0.61	2.57	0.36
512	6.34	0.79	4.00	0.45
2048	9.05	1.05	7.58	0.76
8192	12.32	1.17	8.44	0.78

V	<i>Percentage Dissociation</i>		
	35°	50°	65°
4	42.3	38.3	36.9
8	53.5	50.1	46.9
16	56.5	51.5	49.6
32	61.8	55.8	53.3
128	73.7	66.7	62.9
512	89.4	82.9	79.2
2048	96.6	92.6	92.4
8192	100.0	100.0	100.0

DISCUSSION

Jones and Caldwell,¹ Jones and MacKay² and Jones and Hosford³ have shown by tables that the value for the molecular conductivity of an alum is less than that of the sum of its constituent salts, and that these differences are little affected by rise in temperature. The tables compiled by

¹ Am. Chem. J., **25**, 349 (1901).

² *Ibid.*, **34**, 357 (1905).

³ *Ibid.*, **46**, 240 (1911).

Hosford from earlier work done in this laboratory show further that the differences are smaller the greater the dilution. This is what would be expected since dissociation increases with dilution.

The complexities of the changes of the violet chrome alums into green varieties readily account for their irregularities, but there follow tables which show that in addition to ionization, there is a breaking down of the complex salts into simpler ones. The tables are compiled from the work of Drs. Winston¹ [$\text{Cr}_2(\text{SO}_4)_3$, $(\text{NH}_4)_2\text{SO}_4$, and Na_2SO_4], West² (K_2SO_4) and Hosford³ (NiSO_4):

Table XXVI.—Conductivities of Complex Salts

<i>Ammonium Chromium Sulphate</i>					
V	$\text{Cr}_2(\text{SO}_4)_3$	$(\text{NH}_4)_2\text{SO}_4$	Sum/2	$\text{NH}_4\text{Cr}(\text{SO}_4)_2$	Diff.
8	151	213	182	170	—12
32	230	255	242	229	—13
128	338	292	315	303	—12
512	472	313	392	410	+18
1024	562	323	442	483	+41
2048	708	337	522	577	+55

Potassium Nickel Sulphate

V	K_2SO_4	NiSO_4	Sum	$\text{K}_2\text{Ni}(\text{SO}_4)_2$	Diff.
8	220	93	313	273	—40
32	260	127	387	349	—38
128	297	172	469	432	—37
512	320	219	539	514	—25

Potassium Sodium Sulphate

V	K_2SO_4	Na_2SO_4	Sum/2	KNaSO_4	Diff.
8	220	178	199	200	+1.0
32	260	215	237.5	237	—0.5
128	297	247	272	270	—2.0
512	320	270	295	291	—4.0

Potassium Chromium Sulphate

V	$\text{Cr}_2(\text{SO}_4)_3$	K_2SO_4	Sum/2	$\text{KCr}(\text{SO}_4)_2$	Diff.
8	151	220	185	167	—18
32	230	260	245	226	—19
128	338	297	317	298	—19
512	472	320	395	404	+9

¹ Am. Chem. J., **40**, 368 (1911).

² *Ibid.*, **34**, 357 (1905).

³ *Loc. cit.*

Hydrolysis was noted in several instances and one salt, dipotassium phosphate, showed a time factor.

Jones and MacKay,¹ in their study of the alums, found that the conductivities for certain of the alums were not constant but changed with time. Some of their results are taken from the paper cited.

<i>Sodium Aluminium Alum</i>		
V	Time	Molecular conductivity
20000	0	529
20000	24 hrs.	550
<i>Ammonium Chromium Alum</i>		
2000	0	630
2000	24 hrs.	686
<i>Ammonium Iron Alum</i>		
200	0	320
200	2 hrs.	330
400	0	411
400	20 min.	424
2000	0 min.	694
2000	30 min.	808
2000	18 hrs.	891
2000	21 hrs.	896

When measurements with dipotassium phosphate were made they were found not to agree with those of Miss Winston, and were therefore repeated a week later, when it was found that there was still greater disagreement. At about this time some of the cells were sent away for repairs and it was three weeks before the work could again be repeated. The same mother solution was used and, as the next table shows, for concentrated solutions the variation was again increased. The table shows two things. First, the time factor for hydrolysis is greater for concentrated than for dilute solutions. Second, the temperature has little effect on the time factor. According to the law of mass action, the first would be expected. It is, however, undoubtedly true that a cause of the discrepancies between this work and the earlier work is accounted for in the time required for the hydrolysis equilibrium of the salt.

¹ Am. Chem. J., 19, 105 (1897).

Table XXVII.—*Molecular Conductivities of Dipotassium Phosphate*

Column I. Jones and Winston¹
 Column II. From readings made November 22
 Column III. From readings made November 28
 Column IV. From readings made December 22

V	35°			
	I	II	III	IV
2	138	140	187	198
8	175	184	307	316
32	204	222	332	334
128	230	252		372
512	240	290	420	414
1024	243	276	427	426
2048	243	268	424	422
4096	251	265	424	

V	50°			
	I	II	III	IV
2		175	233	247
8		234	387	401
32		286	422	428
128		322	491	479
512		346	541	533
1024		348	550	545
2048		345	546	545
4096		340	544	

The salts brought within the range of this investigation crystallizing with the largest number of molecules of water are sodium ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$, potassium chromium sulphate, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, potassium nickel sulphate, $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and ammonium chromium sulphate, $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. These salts have the largest temperature coefficients of any of those studied, and at the highest dilutions and temperatures vary between eleven and eighteen conductivity units for each degree. Furthermore, for every salt that did not undergo hydrolysis, the temperature coefficients increased with dilution up to infinite dilution, that is, up to that dilution which showed the greatest molecular conductivity.

¹ *Loc. cit.*

When hydrolysis takes place the temperature coefficients do not increase so regularly with dilution, although, in general, these coefficients become larger with increased dilution. These observations agree with those previously published.¹

Hosford and Jones² have shown that while the violet variety of ammonium chrome alum has a smaller conductivity than the green in more concentrated solutions, in the more dilute the green has the smaller conductivity, the change taking place between $V = 1024$ and $V = 2048$. This is true at lower temperatures. At higher temperatures the values for both the green and the violet varieties are more nearly equal, due probably to a gradual transformation of the violet into the green variety (see Jones and MacKay³).

Monti,⁴ Recoura⁵ and Whitney⁶ have studied the nature of the transformation of the violet chromium sulphate into the green, and undoubtedly the same changes take place in the presence of ammonium and potassium sulphates, that is, in solutions of the alums.

Whatever the interpretation, there is no doubt that a complex ion is formed, made up of SO_4 and Cr. This does not separate into the chromium or sulphuric acid ions, since ammonia will not precipitate all the chromium nor barium chloride all the sulphuric acid. The measurements show that the sum of the conductivities of this complex ion and such others as may be formed is greater than that for the ions from the violet chromium sulphate or the alum.

After the conductivities of potassium permanganate had been measured the cells were found to have been stained brown with manganese dioxide. As the mother solution had been heated to 50° , undoubtedly there was greater decomposition than would have appeared had the solutions been made up originally at, say, 20° . This will account for the lower values obtained at higher temperatures.

¹ Jones: *Am. Chem. J.*, **35**, 450 (1906).

² *Loc. cit.*

³ *Am. Chem. J.*, **19**, 103 (1897).

⁴ *Z. anorg. Chem.*, **12**, 75 (1896).

⁵ *Ann. chim. phys.*, [7] **4**, 494 (1895).

⁶ *Z. physik. Chem.*, **20**, 40 (1896).

The four salts of uranyl that were studied underwent more or less hydrolysis, and therefore agreement was not found with previous workers. Miss Winston¹ observed an increase in percentage dissociation with rise of temperature for uranyl acetate, and attributed the large dissociation to induction. If, as seems possible, there is always a time factor for hydrolysis, this factor would be greater for concentrated than for dilute solutions.

In uranyl acetate the dissociation is greater for higher temperatures only with greater concentrations.

The first table for dipotassium phosphate shows dissociation percentages greater at higher temperatures, but in the second the decrease is seen to be about normal. These measurements, taken, the second a month after the first, show that the greater the interval of time the lower the percentage dissociation. Hence dissociation when measured before hydrolysis is complete does not give concordant results because the more concentrated solutions are less hydrolyzed than the more dilute.

SUMMARY

1. The molecular conductivities have been measured and the temperature coefficients and percentage dissociation calculated for the following salts and acids: Sodium ferrocyanide, potassium carbonate, potassium permanganate, dipotassium phosphate, potassium sodium sulphate, potassium chromium sulphate (violet and green), potassium nickel sulphate, ammonium chromium sulphate (violet and green), calcium bromide, calcium chromate, zinc nitrate, zinc acetate, lead chloride, lead acetate, nickel acetate, uranyl chloride, uranyl nitrate, uranyl sulphate, uranyl acetate, hydrochloric acid, nitric acid and sulphuric acid.

2. Double salts in general have smaller conductivities than the sums of the conductivities of the constituent salts. These differences are little affected by temperature but become less with greater dilution.

3. Certain apparent discrepancies between this work and that of other workers are explained: 1. By hydrolysis with time

¹ *Loc. cit.*

factor. 2. By decomposition such that new substances are formed.

4. The observations of previous workers as to large temperature coefficients for salts that crystallize with large amounts of water were confirmed. For salts that did not undergo hydrolysis the temperature coefficients increased with dilution.

5. The violet varieties of ammonium and potassium chrome alum have smaller conductivities than the green varieties, but the differences become less at higher temperatures.

6. Hydrolysis was noticed in several instances. One salt, dipotassium hydrogen phosphate, had a time factor which extended over days or even weeks.

7. With the exception of uranyl acetate and dipotassium hydrogen phosphate, there was a decrease in percentage dissociation with rise in temperature. After standing four weeks the phosphate acted normally.

BIOGRAPHICAL.

Samuel Francis Howard, the author of this dissertation, was born in Wilbraham, Massachusetts, June 14, 1872. Educated in the public schools of his native town and graduated from Wesleyan Academy (Wilbraham) he entered the Massachusetts Agricultural College in 1891, graduating from that institution in 1894. The next year he was Principal of the Eliot (Me.) High School and in 1896 became enrolled as a graduate student at Johns Hopkins University, remaining until June, 1898. In 1899, he was appointed Assistant Professor of Chemistry at the Massachusetts Agricultural College which position he still holds, having been granted a leave of absence for the past year.

His subordinate subjects have been Physical Chemistry and Physics.

